

3. Supplementary discussion. Raman Scattering in Carbon Nanosystems; Solving Polyacetylene

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More on Herzberg-Teller strength estimates The Herzberg-Teller expansion is simply a Taylor expansion of the transition moment coordinate dependence; it is not a perturbation expansion. The Raman process remains second order in light-matter perturbation theory, including nonperturbative production of phonons.

There is indeed a strong dependence of the propensity to make the π to π^* transition depending on carbon interatomic distance. A simple estimate for the phonon producing capability of the coordinate dependence of the transition moment (non-Condon part of $\mu(\xi)$) as follows: Along a single isolated bond in a very small molecule, a rather commonplace variation of $\mu(x)$ is by about 10% in a 10% bond length change, starting at the equilibrium position of a bond. This typical single bond coordinate dependence needs to be considered in estimating the phonon coordinate dependence of the transition moment. Normalization requires that an extended valence or conduction band delocalized electronic orbital amplitude on a given site is reduced in amplitude by $N^{-1/2}$ compared to orbitals confined to a lone single bond, (later $N \rightarrow \infty$) taking the per-bond contribution to the transition moment

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for a crystal down by a factor of N^{-1} for a given displacement. There are N bonds in the crystal, leaving the net transition dipole strength for the whole crystal, involving the single delocalized valence to conduction band electron transition, of the same order as one electron confined to a single isolated bond.

The phonons are created through the derivatives of the transition moment $\partial\mu(\boldsymbol{\xi})/\partial\xi_{j,q}$, including the zero Γ point phonon modes $q = 0$. The physical displacement per bond is down typically by $N^{-1/2}$ for a unit shift of a normal mode, again due to normalization. We have just seen the per-bond contribution to the transition moment for a crystal already down by a factor of N^{-1} , so the per-bond, valence-to-conduction band state phonon mode derivative of the transition moment is down by $N^{-3/2}$ compared to the analogous transition on a isolated bond. There are N bonds in the crystal, still leaving the transition dipole derivative with respect to a normal mode down by a factor of $N^{-1/2}$, meaning the amplitude of producing a *particular* phonon by the one-electron transition falls as $N^{-1/2}$. The Raman cross section for producing this particular phonon goes as the square of this amplitude, i.e. as N^{-1} . However the phonon density of states in the quasi 1D case increases as N , so the transition strength in any allowed region of k remains stable as $N \rightarrow \infty$. The range of allowed regions increases as the distance between $2q$ and $k = 0$ increases with laser frequency. The increase in total Raman scattering cross section expected with larger molecules tending toward a crystal (increasing N) finally comes when we integrate over all or a finite fraction of the (continuum of) valence to conduction transitions, which provides another factor proportional to N , meaning the total Raman scattering cross section goes as N .

More on the numerical simulation. As stated in the text, the numerical simulation is a phonon (vibration) calculation only, disregarding the difficulties that electron-phonon correlations cause with Pauli blocking and backscattering in the presence of impurities. To do this calculation reliably would be a major quantum chemistry effort, and require knowledge of specific samples. Therefore, we adjusted the strength of the elastic and inelastic sideband parts to demonstrate weak, moderate, and strong backscattering. However the band shape of

both the elastic and inelastic part are natural outcomes of the simulation, only their relative strength is changed arbitrarily. The calculation itself involves a long polymer chain with four random impurities, consisting of mass variations. Harmonic interactions were used between the atoms. For a given random choice of impurities, the phonons were generally found to be localized strongly between one or two pairs of impurities. This causes dispersion in phonon wave vectors and frequencies. It is the average over all these possibilities that give rise to the band shapes of both the elastic and sideband peaks. The side band frequency shift away from the elastic peak also arose naturally in the simulation, as a result of the average dispersion of the lattice and the average wave vector in the simulation. The simulation was done in Mathematica, with 3000 realizations of the impurity positions average for every frame in the figure.

CODE: Sideband and elastic peak study: vibrations in linear chain with alternating bonds lengths, and impurities; using various Fourier information to look at spectral densities after a lot of averaging over impurity location. (as would be true in an experimental sample).

```

disp = {}; siz = 500; (*number of atomic sites*)
For[ipp = 1, ipp < 2600, ipp++, (* ipp is number of trials to be averaged*)
  Hd = ConstantArray[0, {siz, siz}] (*Hd becomes the phonon hamiltonian*)
  For[jj = 1, jj < siz + 1, jj++,
    Hd[[jj, jj]] = -1.1;];
  For[jj = 1, jj < siz, jj++,
    Hd[[jj, jj + 1]] = .5;
    Hd[[jj + 1, jj]] = .5];
  (*increment every other off diagonal coupling mimicking alternating bonds*)
  For[jj = 1, jj < siz, jj += 2,
    Hd[[jj, jj + 1]] = -.1;
    Hd[[jj + 1, jj]] = -.1];
  (* here are set 4 randomly placed impurities*)
  r1 = RandomInteger[{50, 450}];
  r2 = RandomInteger[{50, 450}];
  r3 = RandomInteger[{20, 450}];
  r4 = RandomInteger[{20, 450}];
  Hd[[r1, r1]] += .1;
  Hd[[r2, r2]] += -.1;
  Hd[[r3, r3]] += .1;
  Hd[[r4, r4]] += -.1;
  ss = Chop[Eigenvalues[Hd]];
  eigs = ss[[{1}]; vec = ss[[{2}]; disp2 = {};
  (*tt determines the range we look for sideband shifts*)
  For[tt = 5.02345, tt < 5.024, tt += .0577,
    For[q = siz - 200, q < siz + 1, q++,
      uv = Take[Table[0. + Sin[n (0 + tt) Pi / 500]^2, {n, 1, siz}], siz];
      uv = Take[Table[1 + 1.5 Sin[n (tt) Pi / 500], {n, 1, siz}], siz];
      (*the uv*)
      Table[1 + 2 Sin[n (tt) Pi / 500] represents the transition moment
        oscillations and constant term along the molecular backbone. The
        factors 1 and 2 are arbitrary. changing 2 to 4 say means more
        sideband intensity. The probability for the transition moment
        to activate the qth mode (with the impurities present) is
        (uv.ss[[{2,q}]]^2 That one has an energy of Sqrt[Abs[ss[[{1,q}]]]],
        suitably (but arbitrarily) scaled*)
      disp = Append[disp, {Round[3280 Sqrt[Abs[ss[[{1, q}]]], (uv.ss[[{2, q}]]^2)];
      11]

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(*raw data plot*)
ListPlot[disp, PlotRange → All]
nc = 1;
disp = Sort[disp];
(*process the raw sorting and adding duplicate energie together*)
For[pp = 1, pp < Length[disp] + 1, pp++,
  If[disp[[nc, 1]] == disp[[nc + 1, 1]],
    {disp[[nc, 2]] += disp[[nc + 1, 2]], disp = Drop[disp, {nc + 1}],
    nc += 1}
];
ff = disp[[Length[disp], 1]];
da = Table[0, {k, 1, ff}];
For[op = 1, op < Length[disp] + 1, op++,
  sw = disp[[op, 1]];
  da[[sw]] = disp[[op, 2]];
];
ListPlot[da, PlotRange → {{0, 70}, All}, Joined → True]
ListPlot[MovingAverage[da, 3], PlotRange → {{0, 70}, All},
  Joined → True]
dal += da;
ListPlot[dal, PlotRange → {{0, 70}, All}, Joined → True]
ListPlot[MovingAverage[dal, 3], PlotRange → {{0, 70}, All},
  Joined → True]
ListPlot[MovingAverage[dal, 4], PlotRange → {{0, 270}, All},
  Joined → True]
(*Plot with increasing compression along frequency*)

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Figure 1: Mathematica code for band structure simulations

Significant earlier theories of the Raman spectrum of Polyacetylene Mele's¹ work stands out among the prior attempts to explain the Raman spectrum of polyacetylene.

He remained within second order KHD theory, however making the Condon approximation. Franck-Condon induced potential force changes following photo excitation was the supposed agent driving the spectra, which he called hot luminescence. Except for the term “hot luminescence” this is not unreasonable for smaller molecules or localized orbital regions between defects; the displacements are very likely to mirror the strongest directions of change in the transition moment. The $k = 2q$ rule for sidebands also emerged from this work, which, unfortunately did not get a large following.

Kuzmany and co-workers² also began with KHD theory, but kept only to the “Albrecht A term” which is tantamount to the Condon approximation. They associated electron phonon coupling with excited state coordinate shifts. If the transition is cast onto a single C=C bond, a coupling of about 5,500 wavenumbers is obtained. The 5,500 wavenumber bandwidth is really due to the earliest downhill motion of a nuclear wave packet in the excited state.^{3,4} The steep potential, again cast onto a single C=C bond, certainly is a kind of electron-phonon coupling, but not “scattering”. The authors associated this energy width with an electron decay time of a few femtoseconds, which is probably the right timescale, except for another reason: e-e scattering. Finally these authors were among those resting their case on bi-disperse samples, in this case of 5 and 40 double bonds.

References

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